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eElectrode processes during the electrorefiniment of lead in the KCl-$PbCl_2$-PbO melt

The influence of PbO addition on current efficiency during the electrorefinement of lead in the KCl-$PbCl_2$-PbO melt was investigated. It was shown that with PbO concentration in the KCl-$PbCl_2$ eqiumolar mixture increasing, the current efficiency of lead decreases. Electrode processes mechanism is proposed.

Introduction

Studying of the process of electrochemical recovery of lead from blurred salts in the literature is given considerable attention. Significant contribution to the electrolysis of molten salts in the production of heavy light-fusible metals was made by the scientists of the Ukrainian school of electrochemistry[1–4]. However, the object of the exploration was chloride melts containing no oxygen ions.

Electrolytic behavior of oxide of lead (II) in chloride melts was studied in works by Delimarsky Y.K., Panchenko I.D., and Markov B.F.[5]. The authors conducted electrolysis of the system $PbCl_2$-PbO at temperatures of 500–530 °C and a concentration of PbO to 20 wt%., and showed that there is a possibility of extracting metallic lead from its oxide by electrolysis of molten lead chloride with a current yield of 96–99%.

The aim of this work was to measure cathode current output on lead during the electrorefining of lead in melt KCl-$PbCl_2$-PbO at a temperature of 500 °C depending on the concentration of PbO in the electrolyte.

The experimental part

Schema of the experimental laboratory system is shown in Figure 1.

The lead mark C1 was used as an anode. The cathode was a molybdenum rod

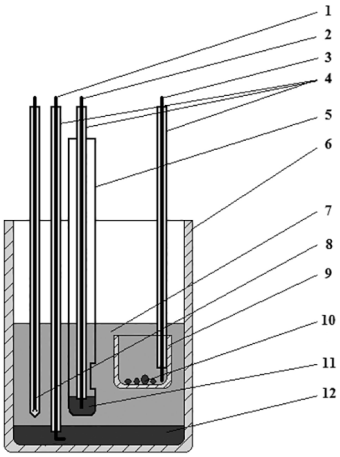

Fig.1. Schema of the experimental laboratory setup:
1 – anode current feeder (Mo); 2 – current source to the reference electrode (Mo);
3 – the cathode of Mo; 4 – corundum tube;
5 – corundum cover the reference electrode;
6 – corundum crucible Ø = 45 mm;
7 – the electrolyte KCl-$PbCl_2$-PbO;
8 – thermocouple in a case of BeO;
9 – corundum crucible Ø = 25 mm;
10 – cathode Pb; 11 – the reference electrode (Pb); 12 – an anode (Pb)

with a diameter of 1 mm and working height of 10 mm *(3)*, shielded with alundum tube *(4)*. To collect the cathode lead to the alundum tube by nichrome wire a cut corundum crucible with a diameter of 20 mm was attached. For the experiments 4 electrolyte compositions KCl-PbCl2-PbO with fixed concentration of PbO 1, 3, 5, and 8 wt. %. were prepared

The temperature of the molten salt was checked with the help of platinum-platinum-rhodium (GD) thermocouple. System of temperature stabilization got its fluctuations during the experiments to within ±2 °C.

For the supply of electric current, sources of DC GWInstekPSW7 30–72 was used; the difference of potentials between the electrodes was measured with multimeter APPA-109 N.

Electrolysis was carried out at 500 °C for 60 minutes in a potentiostatic mode at a potential difference between the cathode and the reference electrode of 0.6 V. At the end of each experiment, the melt was dissolved in drain-mold. From the change in mass of cathodic and anodic lead, cathode and anode current output was determined, based on Faraday's law.

Results and Discussion

During electrolysis, the primary reactions at the cathode are the recovery of lead ions by the reaction:

$$Pb^{2+} + 2e \rightarrow Pb^0 \qquad (1)$$

The main reaction on the anode lead is dissolution by the reaction:

$$Pb^0 - 2e \rightarrow Pb^{2+} \qquad (2)$$

The theoretical value of the mass of dissolved at the anode and obtained at the cathode lead mTeor was determined according to Faraday's law:

$$m_{\text{Teop}} = \frac{A}{z \cdot F} \cdot I \cdot \tau \qquad (3)$$

where A is atomic weight of the metal, g/mole; I is current intensity, A; τ is time, s; z is valence of lead in the electrolyte (based on 2 electrone electrode reaction); F is Faraday constant, 96500 C/mol.

The output of lead current was calculated by the formula:

$$\text{Вт} = \frac{m_{\text{Пр}}}{m_{\text{Teop}}} \cdot 100\% \qquad (4)$$

where $m_{\text{Пр}}$ is metal mass obtained in the course of the experiment, g.

The values of the cathode output current depending on the concentration of

PbO in the melt and a current density are shown in Table 1.

Table 1
Anode current output in depending on the concentration of PbO in the melt

CPbO,% wt.	1	3	5	8
$Bт_K$	96.74	92.87	90.37	86.31
$Bт_A$	98.38	96.74	94.19	91.11

The values of the cathode and the anode output current in all cases is less than 100% based on the two-electron reaction of the electrode. This indicates that even in dilute KCl-$PbCl_2$ on PbO on the surface of the electrodes other electrochemical reactions occur, and the proportion rises with increasing concentration of PbO.

It is worth noting that there was a decrease in the mass of the electrolyte after electrolys that says about the expense of substance.

X-ray results show in the electrolyte melt congealed presence of oxychloride lead compounds Pb_2OCl_2, which in melt may be present in the form of ions $Pb_2O_2^{+6}$.

On the cathode surface after electrolys PbO was found.

From the above stated facts we can assume the following mechanism of electron-electrode processes. Part of PbO oxidized to PbO_2 and shields the anode surface, and a part is deposited at the cathode in conjunction with the lead according to the reaction:

$$Pb_2O^{2+} + 2e \rightarrow Pb^0 + PbO \qquad (5)$$

Fig. 2 shows a photograph of crucible for collection of the cathode lead immediately after the DC disconnect.

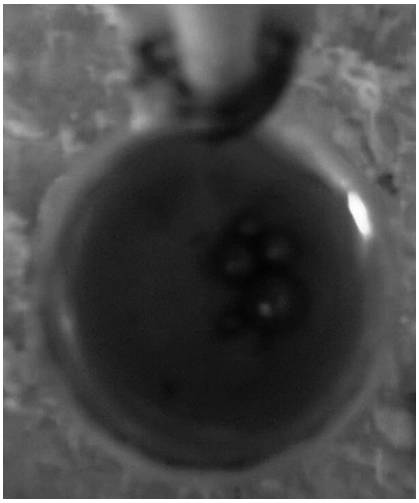

Fig. 2 Photo of the crucible to collect the cathode lead after the DC disconnected. Melt KCl-PbCl2-PbO (8% wt.)

The photograph shows that the recovered lead dropping from molybdenum cathode surface does not form a "puddle", in a substance with a homogeneous surface, but rolled into balls that are not collected in a single body, even with stirring. This suggests that an oxide film is present on the surface of metallic lead formed together with the metal. With its high strength and surface tension, it pulls together the resulting drop in the metal bowl and stirring does not merge into a single body. Part of PbO is the formation of films for metal lead and some remains on the surface of the cathode. Depending on the concentration of PbO in a chloride melt deposited oxide can again dissolve in the melt with a low concentration of PbO, and saturated monoxide melt will lead to the cathode surface, or be present in the sheath of the cathode space.

Conclusions

1. Experimentally determined values of the cathode and anode output current lead in the electrorefining of lead oxide-chloride melt KCl-$PbCl_2$-PbO.

2. It is shown that the cathode and the anode output current are not equal 100% in all experiments.

3. With an increase in concentration of PbO in melt KCl-$PbCl_2$-PbO cathodic current efficiency decreases from 96.7% to 86.31%, and the anode current efficiency declines from 98.38 % to 91.11%.

4. X-ray analysis shows the presence of an electrolyte oxychloride Pb_2OCl_2.

5. Metallic lead obtained on molybdenum cathode drops and takes a spherical shape that signifies the presence of a solid oxide film on lead surface formed simultaneously with the metal lead.

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